POLYSACCHARIDE DERIVED HYDROGEL BEADS FOR APPLICATIONS IN ENVIRONMENTAL AND AGRICULTURAL FIELDS

SYNOPSIS

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The thesis entitled "Polysaccharide Derived Hydrogel Beads for Applications in Environmental and Agricultural Fields" deals mainly with the synthesis, characterization and applications of hydrogel beads. The work is divided into five chapters.

CHAPTER I	**:**	**Review on recent developments in environmental and agricultural applications of guar gum and cellulose acetate-based hydrogels**
CHAPTER II	**:**	**Preparation and characterization of polyethylene glycol crosslinked guar gum hydrogel beads for the adsorption of pesticide chlorpyrifos**
CHAPTER III	**:**	**Fabrication and characterization of polyethylene glycol crosslinked cellulose acetate hydrogel beads for the adsorption of pesticide chlorpyrifos**
CHAPTER IV	**:**	**Agricultural applications of guar gum and cellulose acetate hydrogel beads**
CHAPTER V	**:**	**Preparation and characterization of carbon dots incorporated hydrogel beads**

Chapter 1: Review on recent developments in environmental and agricultural applications of guar gum and cellulose acetate-based hydrogels

A hydrogel is a three-dimensional (3D) network of hydrophilic polymers that can swell in water and hold a large amount of water while maintaining the structure due to chemical or physical cross-linking of individual polymer chains [1]. The hydrophilicity of the network is due to the presence of hydrophilic groups such as -NH_2, -COOH, -OH, -$CONH_2$, -CONH-, and -SO_3H. Hydrogels can be classified into two distinct categories, the natural and the synthetic hydrogels. Natural hydrogels include collagen, fibrin, hyaluronic acid, matrigel and derivatives of natural materials such as chitosan and alginate. Synthetic hydrogels such as poly (ethylene glycol) diacrylate, poly(acryl amide), poly(vinyl alcohol) are more reproducible, although their final structure can also depend on polymerization conditions [2].

Hydrogels are incredibly well-suited for loading substances which are water soluble due to their high porous nature, soft texture and the most delicate three-dimensional network [3]. Additionally, the biodegradable gels known as hydrogels have interconnected pores that are extremely important to the adsorption process. The pores can be permanently altered by the following methods: (i) integrating nanoparticles [4] (ii) lyophilization [5] (iii) grafting mechanism [6] (iv) cryogelation [5] and (v) cross-linking polymerization [7]. Guar gum is a polysaccharide made up of galactose and mannose monomers. It has a linear chain made of β 1,4-linked mannose residues to which galactose residues are 1,6-linked at every second mannose, forming short side branches. It has been observed that gum polysaccharide graft co-polymers maintain the biodegradable nature of the original gum polysaccharides and show superior qualities needed for a variety of applications, including wastewater treatment [8]. The application of guar gum has expanded dramatically in recent years, particularly in paints, oils and cosmetics. It is observed as an additive in papermaking, emulsifying agent, suspending and wound healing. Guar gum is used as an adsorbent with various modifications using different crosslinkers for the adsorption of dyes, pesticides and heavy metals [9].

Among the natural polymers, cellulose is abundantly available and could be easily isolable also [10]. The beads obtained from cellulose-based polymers could be named as beaded cellulose, microspheres, pearl cellulose, cellulose gels or pellets. These beads exhibit biocompatibility and super absorbent capacity to find use in drug delivery, tissue healing and environmental remedies [11]. The beads fabricated out of synthetic polymers, like polyethylene glycol (PEG), polyacrylamide (PAM) and polyvinyl alcohol (PVA), show excellent qualities though they were

not well accepted due to their inherent toxicity. Hence, the hydrogel beads made out of biopolymers like chitosan, alginate or cellulose would fit as better alternatives due to their excellent polymer characteristics and low toxicity [12]. The most important ester of cellulose, the cellulose acetate (CA) used as a bio-adsorbent material owing to its superior properties than cellulose; like good mechanical strength, permeate flux and excellent antifouling due to hydrophilic nature of CA [13]. The acetyl and hydroxyl groups of CA beads facilitate the binding of metal ions to the beads, which is why they are typically employed to extract metal ions from water [14]. The use of CA beads for the removal of pesticides has not documented so far. So, the more abundant cellulose-based adsorbing materials and guar gum could be of right selection for the applications carried out in the present work.

Research gap

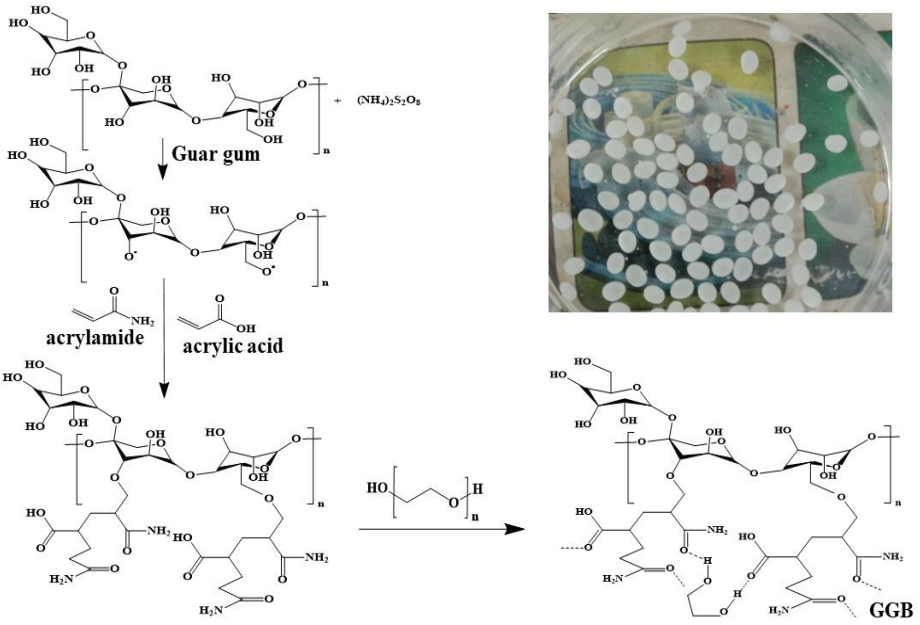
Based on the literature review, it was found that the hydrogel beads have been studied for their ability to adsorb chlorpyrifos, the specific interactions between the hydrogel's polymeric structure and chlorpyrifos molecules are not fully understood. There is a lack of detailed information on how different functional groups in hydrogel beads interact with chlorpyrifos. So, the present work is proposed to prepare and characterize the hydrogel beads which are applied in the adsorption process, as fertilizer-coated superabsorbent for plants and adsorption of heavy metals. The detailed information on the interactions between functional groups of hydrogel beads and chlorpyrifos has been explained.

Research objectives

- To prepare and characterize polyethylene glycol crosslinked guar gum hydrogel beads for the adsorption of pesticide
- To fabricate and characterize polyethylene glycol crosslinked cellulose acetate hydrogel beads for the adsorption of pesticide
- To synthesize and characterize guar gum and cellulose acetate-based fertilizer-encapsulated beads for agricultural applications
- To synthesize and characterize carbon dots incorporated guar gum and cellulose acetate hydrogel beads for the adsorption of heavy metals

Chapter 2: Preparation and characterization of polyethylene glycol crosslinked guar gum hydrogel beads for the adsorption of pesticide chlorpyrifos

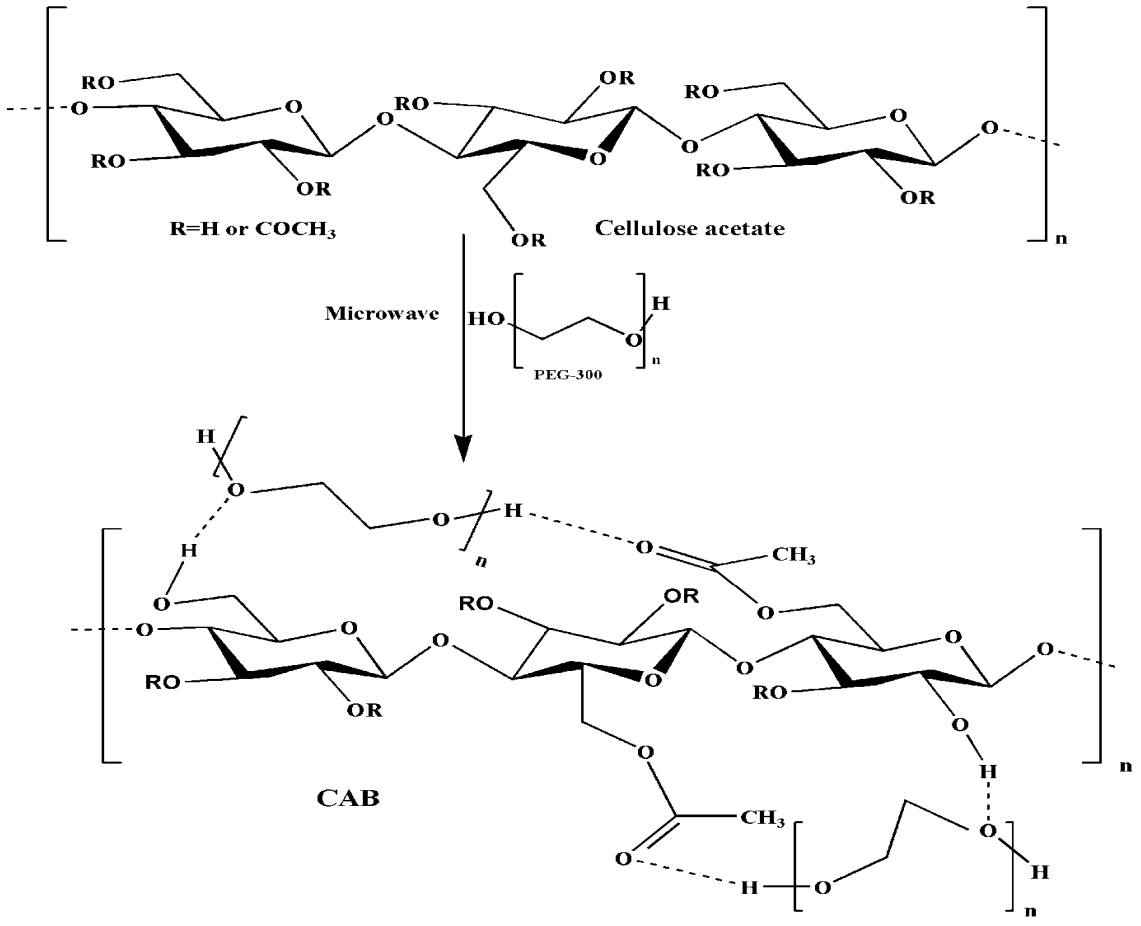
The present chapter deals with the fabrication of guar gum-polyethylene glycol hydrogel beads (GGB) by dropping method from an aqueous solution of guar gum (GG) using ammonium persulfate (APS) and polyethylene glycol (PEG) as initiator and crosslinker respectively, for the adsorption of chlorpyrifos (CP) from water. The semi-crystalline nature of the synthesized beads was confirmed by FESEM analysis. The TGA studies implied that the beads were thermally stable up to 600 °C. The maximum swelling ratio of 1400 gg^{-1} was attained at pH 9.2 and 80 min. The evidence of a strong absorption band was found in FTIR spectrum at 584 cm^{-1} due to -P=S of the adsorbed pesticide CP. The maximum adsorption of CP was found to be 220.97 mgg^{-1}. The adsorption followed pseudo second-order kinetics and Langmuir adsorption isotherm with regression coefficients 0.9998 and 0.9938 which followed the chemisorption process. It is due to the hydrolysis of CP at pH 9.2 to yield 3,5,6-trichloropyridinol which in turn reacts with the carboxylic group present in GG giving -N-C=O linkage. The free energy change $-\Delta G^0$ indicates that the process is spontaneous and involves chemisorption which is thermodynamically and kinetically favorable and a $-\Delta H^0$ value (-10.37 kJ/mol) suggests that the adsorption is exothermic. The adsorption-desorption cycles indicate that the percentage of desorption was high for five cycles with a very small decrease in the adsorption and desorption capacities over the course of several cycles. Scheme 1 depicts the mechanism for the synthesized hydrogel.



Scheme 1: Mechanism for the formation of Guar gum-PEG hydrogel beads (GGB)

Chapter 3: Fabrication and characterization of polyethylene glycol crosslinked cellulose acetate hydrogel beads for the adsorption of pesticide chlorpyrifos

This chapter reports the synthesis, characterization and application of cellulose acetate-polyethylene glycol hydrogel beads (CAB) by dropping method. The hydrogel was synthesized by crosslinking polyethylene glycol (PEG) with cellulose acetate (CA) using microwave irradiation. The hydrogel beads formed were thermally stable and of semi-crystalline nature confirmed by TGA, FESEM and XRD analysis. The maximum swelling ratio of 250 gg^{-1} was attained at pH 7.3 and 480 min with a maximum adsorption capacity of 357.14 mgg^{-1}. The adsorption process followed pseudo second-order kinetics and Langmuir isotherm with regression co-efficient values as 0.9924 and 0.9921 indicating chemisorption. The chemisorption occurred by the nucleophilic attack of the hydroxyl group of cellulose acetate- polyethylene glycol hydrogel beads (CAB) on -P=S of CP expelling 3,5,6-trichloropyridinol (TCP)**.** This was also evidenced by the presence of an absorption band due to -P=S (699 cm^{-1}) in the CP adsorbed CAB (CPCAB). Further, the desorption occurred at pH 1.3 by the acid hydrolysis with 99% recovery up to three cycles. Scheme 2 represents the synthetic route of the prepared hydrogel.

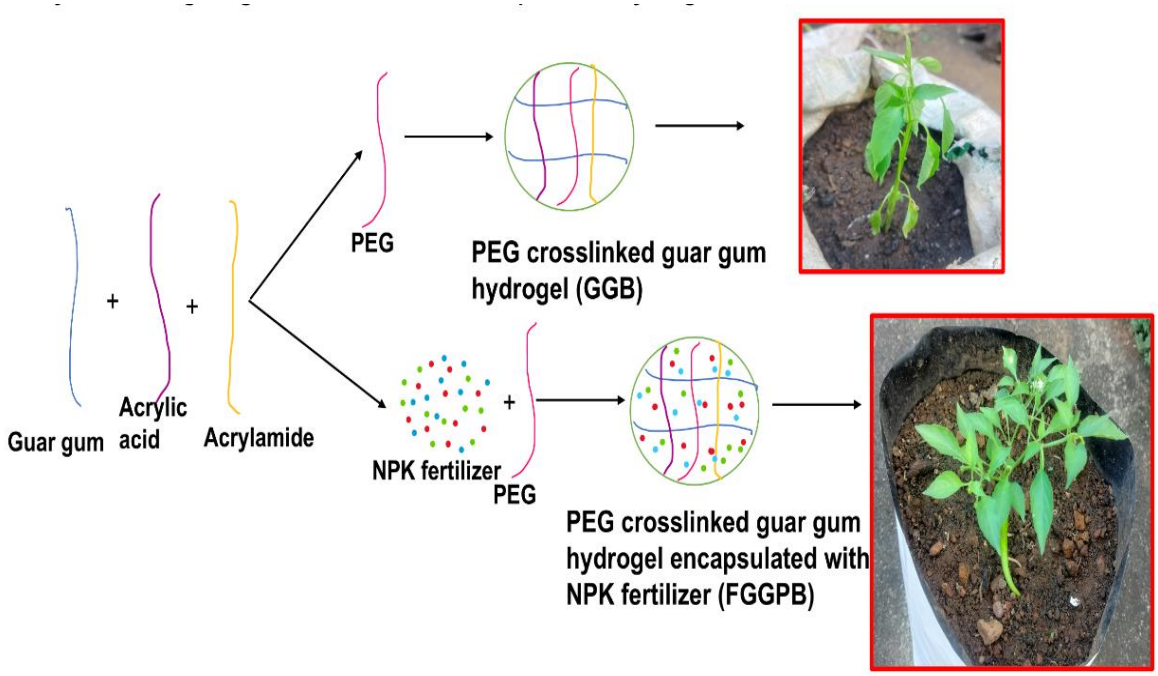


Scheme 2: Mechanism for the formation of cellulose acetate-PEG hydrogel beads (CAB)

Chapter 4: Agricultural applications of guar gum and cellulose acetate hydrogel beads

IV A: Guar gum hydrogel beads for controlled release of fertilizers

This chapter highlights the study on the synthesis, characterization and agricultural applications of guar gum-polyethylene glycol beads (GGB) as well as guar gum beads coated nitrogen, phosphorous and potassium (NPK) fertilizer. The beads were synthesized using the crosslinking agent polyethylene glycol using drop cast method. The newly fabricated beads were characterized by FTIR, FESEM and swelling studies. Water retention, water holding, and soil porosity tests were conducted using GGB. The results showed that the swelling ratio for GGB was 350 g/g. At high pressures, GGB retained 20% more water than untreated soil and the water-holding capacity of soil improved to 16.05% whereas the porosity of soil increased to 69.45% when compared to untreated soil. The biodegradable studies of the hydrogel beads showed that GGB was more susceptible to degradability since it was a natural polymer. The slow release of fertilizers was checked using dissolution studies as *in-vitro* analysis and then the beads were taken into the field to check the growth in the real samples. It was seen that PEG crosslinked GG coated with NPK were highly efficient than the uncoated beads. The synthetic route has been shown in scheme 3.

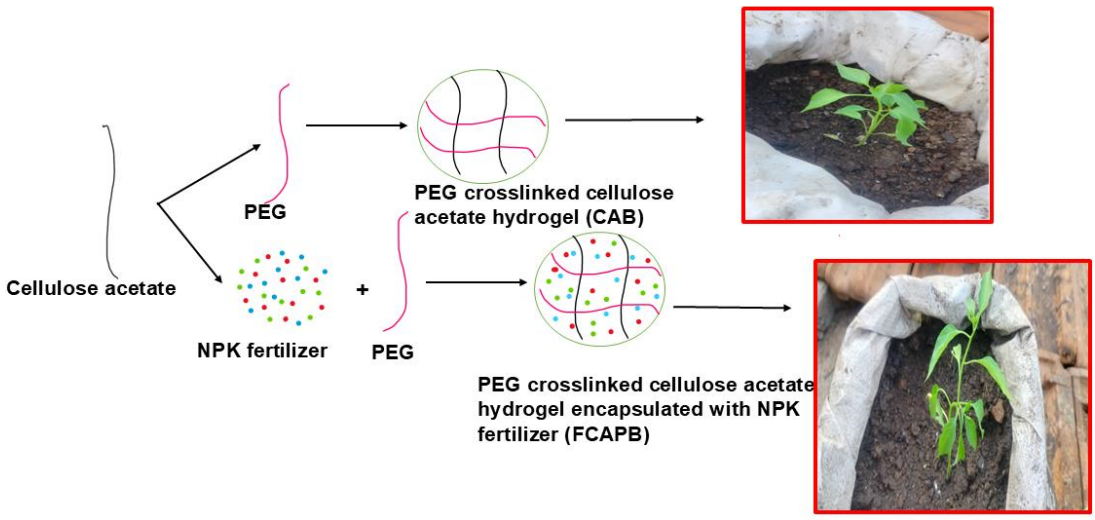


Scheme 3: Synthetic route for the formation of fertilizer-encapsulated and non-encapsulated beads

IV B: Cellulose acetate hydrogel beads for controlled release of fertilizers

This chapter highlights the study on the synthesis, characterization and agricultural applications of cellulose acetate-polyethylene glycol beads (CAB) as well as guar gum beads coated NPK

fertilizer. The beads were synthesized using the crosslinking agent polyethylene glycol using drop cast method. The newly fabricated beads were characterized by FTIR, FESEM and swelling studies. Water retention, water holding, and soil porosity tests were conducted using CAB. The results showed that the swelling ratio for CAB was 250 g/g. The controlled release of NPK fertilizer was studied by *in-vitro* and *in-vivo* analysis. The research emphasized the promise of cellulose acetate-based fertilizer encapsulated hydrogel beads as a viable method for the regulated release of fertilizers. The cellulose acetate-polyethylene glycol hydrogel beads demonstrated excellent swelling and water retention properties, whereas cellulose acetate-based fertilizer encapsulated hydrogel beads demonstrated a slow and steady release of vital nutrients such as nitrogen, phosphorus and potassium. The synthetic route has been shown in scheme 4.



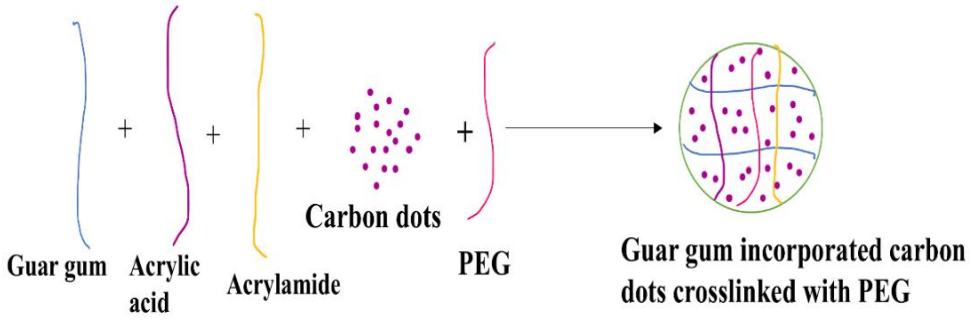
Scheme 4: Synthetic route for the formation of fertilizer-coated and uncoated beads

Chapter 5: Preparation and characterization of carbon dots incorporated hydrogel beads

5 A: Guar gum hydrogel beads for the adsorption of heavy metals

The present chapter reports a study on the removal of heavy metals by the use of carbon dots (CDs) incorporated guar gum hydrogel beads. The hydrogel beads were synthesised by dropping method using polyethylene glycol as crosslinker. The CDs were prepared using urea and citric acid in a ratio of 1:1. The synthesized beads were characterized for their morphology using field emission scanning electron microscopy (FESEM) and the structural elucidation was done using Fourier transform infrared (FT-IR) spectroscopy. The FTIR spectra showed bands centered at 3375 cm^{-1}, 3195 cm^{-1}, 1646 cm^{-1}, 1431 $cm^{-1}$and 1055 cm^{-1}. These bands reveal the surface functional groups present at the CDs. UV-vis spectra were also measured using a UV-vis spectrophotometer (UV-2600, Shimadzu Co., Japan) with a scanning region between 300 and 900 nm and the

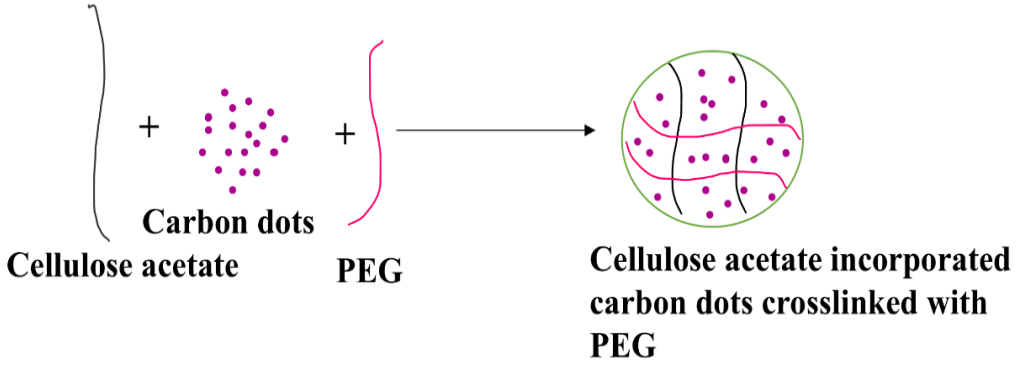
fluorescent features were observed using a fluorescence spectrophotometer. Adsorption processes were carried out for the removal of heavy metals Fe^{3+}, Ba^{2+}, Pb^{2+} and Cu^{2+}. The remaining concentrations of all the aqueous solutions were measured by using atomic absorption spectrometry (AAS). The synthetic pathway is shown schematically in the scheme 5.



Scheme 5: Synthetic pathway for the formation of GG incorporated carbon dots crosslinked with-PEG.

5 B: Cellulose acetate hydrogel beads for the adsorption of heavy metals

The present chapter reports a study on the removal of heavy metals by the use of CDs incorporated hydrogel beads. The hydrogel beads were synthesized by dropping method using polyethylene glycol as crosslinker. The CDs were prepared using urea and citric acid in a ratio of 1:1. The synthesized beads were characterized for their morphology using field emission scanning electron microscopy (FESEM) and the structural elucidation was done using Fourier transform infrared (FT-IR) spectroscopy. The FTIR spectra showed bands centered at 3415 cm^{-1}, 2928 cm^{-1}, 1756 cm^{-1}, 1402 $cm^{-1}$and 1247 cm^{-1}. These bands show the surface functional groups present on the CDs. UV-vis spectra were also measured using a UV-vis spectrophotometer (UV-2600, Shimadzu Co., Japan) with a scanning region between 300 and 900 nm, and the fluorescent features were observed using a fluorescence spectrophotometer. Adsorption processes were carried out for the removal of heavy metals Fe^{3+}, Ba^{2+}, Pb^{2+} and Cu^{2+}. The remaining concentrations of all the aqueous solutions were measured by using atomic absorption spectrometry (AAS). The synthetic pathway is shown schematically in the scheme 6.



Scheme 6: Synthetic pathway for the formation of CA incorporated carbon dots crosslinked with-PEG

Research outcome

- The novel CA and GG hydrogel beads were synthesized which was used for the adsorption studies
- The CA and GG hydrogel beads were coated with NPK fertilizer and the agricultural applications were studied using the beads
- The CA and GG were incorporated with carbon dots and the beads synthesized were applied in the adsorption experiments
- All the modified forms of hydrogel beads were primarily characterized by different analytical techniques

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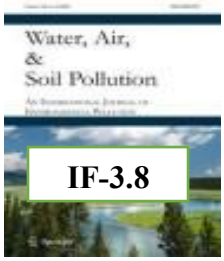
LIST OF RRSEARCH PAPERS PUBLISHED IN JOURNALS AND PRESENTED IN CONFERENCES

1. **M. Nishitha,** B. Narayana, B. K. Sarojini, "Studies on guar gum and cellulose acetate superabsorbent hydrogel beads with high water retention properties for rejuvenation of dryland wettability," *Indian Journal of Chemical Technology*, 31(3) (2024), 425–437 https://doi.org/10.56042/ijct.v31i3.6339.

2. **M. Nishitha,** B. Narayana, B. K. Sarojini, B.S. Dayananda, "Fabrication and characterization of biodegradable hydrogel beads of guar gum for the removal of chlorpyrifos pesticide from water," *International Journal of Biological Macromolecules*, 277 (2024), 134454, https://doi.org/10.1016/j.ijbiomac.2024.134454.

3. **M. Nishitha,** B. Narayana, B. K. Sarojini, A. K. Kodoth, "Environmentally benign cellulose acetate hydrogel beads for solid phase extraction of chlorpyrifos pesticide from water", *Water. Air & Soil Pollution, WATE-D-23-02438R1*



4. M. Nishitha, B. Narayana, B. K. Sarojini, A. K. Kodoth, "Environmentally benign cellulose acetate hydrogel beads for solid phase extraction of chlorpyrifos pesticide from water", International Conference on Functional Materials for Advanced Technology (ICFMAT-1), Department of Physics, Central University of Kerala, 2-4 January 2023.

5. M. Nishitha, B. Narayana, B. K. Sarojini, "Studies on guar gum and cellulose acetate superabsorbent hydrogel beads with high water retention properties for rejuvenation of dryland wettability", National Conference on Condensed Matter Physics and Applications [CMPA 2023], Department of Physics, Manipal Institute of Technology, 14-15 December 2023.

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